Cr(VI) and Dye Biosorption in Batik Wastewater using Biosorbent in The Tea Bag

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Abstract. Cr(VI) and dye contents on batik wastewater has been reduced by biosorption using cheap, abundant, and easily obtained biosorbent such as *Sargassum cinereum* and *Pleurotus ostreotus* baglog waste. Biosorbent in the tea bags can increase adsorption capacity because it has a large surface.This research aims to obtain the optimum of biosorbent ratio and particle size in the tea bag package to Cr(VI) adsorption and decolorization. This experimental research was conducted using Spilt Plot Design. The obtained data were analyzed using anova test on 5% significane level. Based on result study, the highest of Cr(VI) adsorption found at the biosorbent in the tea bag with ratio of 3:1 and particle size of 250-425 μm i.e. 0,0042 mgg^{-1} with reduction efficiency was 68,31%. Percentage of decolorization was 39,92% found at biosorbent in the tea bag with ratio 0:1 and particle size of 425-675 μm. Biosorbent in the tea bag was effective to reducing Cr(VI) and dye in batik wastewater.

Keywords**: biosorption, batik wastewater, Cr(VI), dye, tea bag**

1. Introduction

Batik wastewater generated from washing, coloring and dyeing processes. It contains pollutant such as heavy metal and dyes. Without appropriate treatment, batik wastewater may cause severe environment pollution. Moreover, it is very common in Indonesia that the small-scale batik industries clustered in a certain area such as in Sokaraja Batik Center, Central Java, with their wastewaters, are directly discharged to the environment, i.e., Wangan River. As a result, heavy metal concentration, e.g., Cd 0.018 mgL^{-1}; Cr 0,231 mgL^{-1}; Pb 0.033 mgL^{-1} and Cu 0.025 mgL^{-1}[1]has exceended the treshold values ascertaintained by goverment regulation No. 82 of 2001.

Heavy metal and dye contents in batik wastewater can minimize by biosorption. Biosorption is adsorption using inactivated or dead organisms[2]. Biosorption is greatly effective to adsorb heavy metals and dyes in waste due to the relatively simple, cheap, high adsorption rate, and selective[4-6].

Indoneisa as a mega biodiversity country has many spesies that have the potential as biosorbent. Biosorption is an alternative technology, so the biosorbent used must be abundant, easily available, cheap and ecofriendly. *Sargassum cinereum* and *Pleurotus ostreatus* are potential spesies as biosorbent. The use *S. cinereum* and *P. ostreatus* as biosorbent can produce low carbon emissions thus supporting the realization of low carbon development. *S. cinereum* has latex membrane in their cell wall which contains alginate. It can act as an efficient heavy metal ion exchanger[6]. *P. ostreatus* (oyster mushroom) is a white rot fungus which able to remove odor, degrade stain, and adsorp heavy metals[7]. *P. ostreatus* have high economic value, so it is unappropriated to use as directly heavy metals adsorber, but it utilized after being discharged from mushroom culture (*baglog*).

Biosorption efectivity is highly dependent on biomass, contact time, and biosorbent surface[8]. High biomass and biosorbent surfaces will increase the number of available active sites for binding of the heavy metal ions so highly adsorption capacity. Method to increase adsorption capacity is surface resized the biosorbent. Some forms of biosorbent have been widely applied to adsorb heavy metals and dyes in the environment, such as biosorbent immobilized silica gel[9], biomass size 1 cm[10], powder[11] and pellet[12]. All forms of biosorbent are effective but difficult to separate the waste. Biosorbent packaged in tea bag can be easily separated from the solution system when it is applied and doesn't cause sedimentation. For that reason, the aim of study is to get the optimum biosorbent ratio and particle size in the tea bag to adsorb chromium and decolorize batik waste water.

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2. Research Method

2.1. Material and Method

This experimental research was conducted using Spilt Plot Design. The main plot was the mixture ratio of *S. cinereum* and *P. ostreatus* baglog wastes and as sub plot was the biosorbent particle size. The ratio of *S. cinereum* and baglog wastes consisted of five levels (1:0; 3:1; 1:1; 1:3 and 0:1) while the particle size of the biosorbent consisted of three levels (150-250; 250-425 and 425-675 µm).

2.2. Biosorbent in Tea Bag Package

Biosorbent has weighed as much as 500 mg with the composition according to treatment. Biosorbent was wrapped with tea bag paper by the size of 4 x 6 cm. Biosorbent was packed in the tea bags and ready to use.

2.3. Batik Wastewater Preparation

The wastewater tooks from the Sokaraja Batik Center in Sokaraja Kulon Village, Sokaraja Subdistrict, Banyumas Regency, Central Java Provinsi. The used wastewater was the final waste of staining and dyeing residual. The initial pH of waste set to 8.

2.4. Adsorption Experiments at Laboratory Scale

Erlenmeyer 250 mL provided as many as 45 pieces; each erlenmeyer filled 100 mL of batik wastewater. Each erlenmeyer was added one packed biosorbent in the tea bag with the composition and particle size according to treatment. Erlenmeyer covered with paraffin. It homogenized in the shaker incubator at speed of 175 rpm and temperature of 25^{0}C for 1 hour.

2.5. *The* Chromium Adsorption Capacity

Adsorption capacity calculated by formula:

$$q=\frac{V\,(C_o-C_{eq})}{m}$$

q = Adsorption capacity (mgg^{-1})
V = volume of solution (L)
M = biosorbent weigth (g)
C_o = initial concentration (mgL^{-1})
C_{eq}= final concentration (mgL^{-1})

2.6. Decolorization Percentage

Decolorization percentage measured at each interval treatment using the spectrophotometric method. Batik wastewater before and after treatment taken about 5 mL, then centrifuged at speed of 5,000 rpm for 10 minutes. The supernatant obtained then measured by absorbance using a spectrophotometer at wavelength of 645 nm. Decolorization percentage calculated using the formula:

$$\%\ decolorization=\frac{\text{the initial absorbance - the final absorbance}}{\text{the initial absorbance}}\ \text{X}\ 100\%$$

2.7. Analysis Method

The obtained data was the Cr(VI) adsorption and decolorization percentage. Data was analyzed using an anova test on 5% significant level to determine the effect of treatments.

3. Result and Discussion

The result show that chromium concentrantion of batik wastewater before and after biosorption are different. Cr(VI) adsorption capacity depend on the ratio and particle size of biosorbent in the tea bag. At the optimum adsorption condition, i.e in initial pH of batik wastewater 8 and contact time 1 hour, Cr(VI) concentration after biosorption ranged from 0.0028 - 0.00515 mgL^{-1}. The highest Cr(VI) adsorption capacity found at the biosorbent in the tea bag with ratio of 3: 1 and particle size of 250-425 µm i.e.0.0042 ± 0.0005 mgg^{-1} (Fig.1) with reduction efficiency of 68.31% from the initial concentration of 0.024 to 0.003 mgL^{-1}. The lowest Cr(VI) adsorption capacity found at the biosorbent in the bag with ratio of 1: 1 and particle size 425-675 µm i.e. 0,0028 ± 0.0006 mgg^{-1} with reduction efficiency of 59.84% from initial concentration of 0.019 to 0.005 mgL^{-1} (Fig.1).

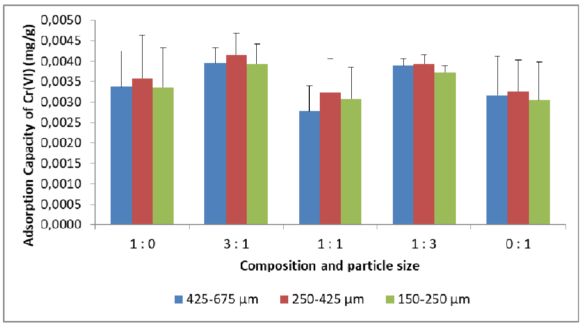

Fig.1. The Cr(VI) adsorption capacity using biosorbent in tea bag

Based on Fig. 1, Cr(VI) adsorption capacity in all composition ratios of the biosorbent in the tea bag increased from the particle size of 250-425 µm to 425-675 µm, then decreased on the particle size of 150-250 µm. The increasing expected because the smaller of particle size can expand the biosorbent surface so that more active sites are on the cell wall to bind more metal ions. The Cr(VI) adsorption decreasing on particle size of 150-250 µm due to the active site has been saturated with Cr(VI) ion so that additional of the biosorbent surface area can't increase the Cr(VI) adsorption because of the desorption process. Desorption occurs due to the active site or empty cavities have been filled entirely or has been saturated so no longer able to perform adsorption[13]. The adsorped Cr is released during the shaking proses and separated from the surface of the biosorbent cell wall[14]. The adsorption in a single layer will only provide one active site to one molekul[15]. Biosorbent in the tea bag less effective than pellet which have acid fuchsin adsorption capacity 181.82 mgg^{-1} [12]. Biosorbent in the tea bag clump when contact with the waste. It causes the effectiveness of adsorption decreases. The low Cr(VI) adsorptionof biosorbent in the tea bag at paticle size 150-250 µm also suspected by reducing of biomass because of the presence leakage of biosorbent from the tea bag. It is in accordance with the weigth data of biomass at the particle size 150-250 µm was consistently smaller than the initial weigth before adsorption, i.e. 438,33 mg (Fig 2.).

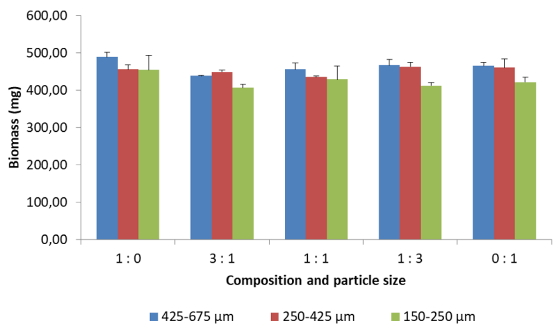

Fig. 2. Weigth of biosorbent in the tea bag after usage

Based on Fig. 2, it is clear that the utilization three particle size to the lost of weigth of biosorbent, especially for the biosorbent with particle size 150-250 µm. During shaking, it is predicted that some particles of biosorbent are escape through the pore of tea bag. Its assumed that the tea bag pore size is smaller than 150-250 µm. The smaller biosorbent particle size, the greater chance of qualifiying from the dye bag.

In addition, for adsorp heavy metals, biosorption can also decolorize dyes contained in the batik wastewater. The highest decolorization i.e., 39.92% found at biosorbent in the tea bag with ratio of 0:1 and particle size 425-675 µm while the lowest found at biosorbent in the bag with ratio of 1:0 and particle size 150-250 µm, i.e., 34,51% (Fig. 3).

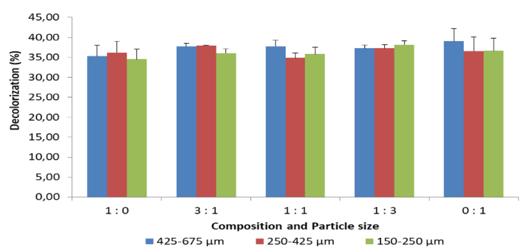

Fig. 3. Decolorization of batik wastewater by biosorbent in the tea bag

Based on Fig. 3. biosorbent at all particle size gave a relatively low percentage of decolorization. It is due to the many combinations of synthetic dyes used by craftsmen batik. The use of unclear dye dose can also inhibit dye degradation in wastewater. Biosorption experiments were optimized to adsorp Cr(VI), resulting in low dye degradation

Biosorption process is one of removal mechanism of heavy metal ions passively[16] which occur on the cell wall. The mechanism of biosorption through the exchange monovalent and divalent ions such as sodium, magnesium and calcium with metal ions and the formation of functional complex molecules with heavy metal ions. Functional molecules in the cell wall include carbonyl, amino, hydroxyl, phosphate, and carboxyl. The active process is occured simultaneously in line with the metal ion consumption and intracellular accumulation of metal ion.

Based on analysis variance, the particle size of biosorbent in the tea bag has the significant effect to Cr(VI) adsorption capacity. It showed that Cr(VI) adsorption doesn't affected by the mixer ratio of *S. cinereum* and *P. ostreatus* baglog waste but affected by particle size. Based on LSD test (Table 1), all particle size have same effect to Cr(VI) adsorption capacity, but particle size of 250-425 µm has the highest adsorption, i.e. 0.0109 mgg^{-1}.

Table 1. LSD value of particle size to Cr(VI) adsorption capacity

Particle Size (µm)	Cr(VI) adsorptin capacity (mgg^{-1})
425-675	0.0103a
250-425	0.0109a
150-250	0.0103a

Note: numbers followed by the same letter doesn't different based on LSD at 95% confidence level

The absorption difference influenced by compound concentration in biosorbent. *S. cinereum* has the active site of metal ion binding in the form of latex membrane (masilag) containing alginate that is pure polymer from uronat acid which arranged in a long linear shape[17]. Alginic acid is composed of D-Manuronic acid and L-Guluronic[18]. *S. cinereum* alginic shape is in the form of a salt derivative called alginate. Alginate consists of sodium alginate, potassium alginate and ammonium alginate which insoluble in the water. Alginate is a polysaccharide that contained in the seaweed talus. Alginates contained in an external cell wall of seaweed is a ligand group that negatively charged because it has a carboxylic acid formation on uronat acid to bind heavy metal[19].

P. ostreatus baglog waste has known having potential as adsorption material because they contain cellulose and hemicellulose[20-21]. *P. ostreatus* baglog waste still have some content such as mycelium and cellulose. Its can decolorization batik wastewater. The mycelium fungus is known to be able to absorb the dye contained in batik waste with enzymatic and non-enzymatic. The fungal mycelium is hydrophobic during the hydrophilic dye, so that the interaction between the hydrophobic-hydrophilic fungal mycelium and dyes[22]. The adsorption process by mushroom mycelium an initial rate of color change, the next process is enzymatical. Decolorization enzymatically to produce extracellular enzymes by fungi. *P. ostreatus* fungus known to produce enzymes ligninolitik i.e. laccase , lignin peroxidase and manganese peroxidase to decolorize. The enzymatic mechanism was to dissolve the chromophore group or cluster color poster. *P. ostreatus* baglog waste contains cellulose which allegedly has decolorization. Sawdust containing cellulose can absorp the dye textiles[23]. The content of cellulose contained in the *P. ostreatus* baglog waste affecting decolorization on batik waste generated so that the percentage is also high.

4. Conclusion

The optimum ratio and particle size of biosorbent in the tea bag to chromium adsoption in batik wastewater was 3: 1 and 250-425 µm and those to decolorize was 0: 1 and 425-675 µm. Respectively biosorbent in tea bags is effective but clumping occurs when contact with the waste.

5. Reference

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